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GAS-PHASE PHOTOELECTRON SPECTROSCOPY OF METALS AND  
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DEPT OF CHEMISTRY J M DYKE 01 OCT 87 AFOSR-TR-87-1634  
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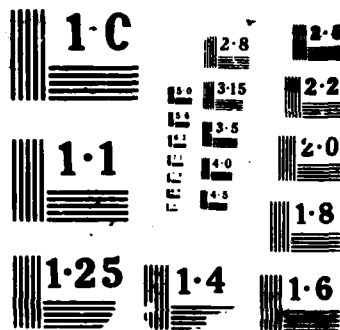
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>Photoelectron spectroscopy is used to study in the gas phase the electronic structure of metals and metal oxides which are of importance in the upper atmosphere. Ionization energies and cross-sections at discrete wavelengths are obtained. Exothermicities of charge exchange reactions of metal oxides and dioxides of importance to atmospheric modelling calculations will be determined.</b>			

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The main objective of this research was to use vacuum ultraviolet photoelectron spectroscopy to study the electronic structure of a number of metals and metal oxides which are of importance in the upper atmosphere. High temperatures are required to produce the species of interest in the vapour phase and these were achieved with radio-frequency induction heating of a thin walled furnace containing a solid sample. The maximum temperature available was 3000 K. Experiments were performed both with a single detector high temperature photoelectron spectrometer and a recently developed multidetector instrument.

Observation of the photoelectron spectra of a metal and its metal oxide allows ionization energies to be determined accurately, relative photoionization cross-sections to be estimated and, for molecular species, if vibrational structure is observed, details of the ionic potential surface can be obtained. Of particular interest are the metals and oxides of the transition metals, lanthanides and actinides as well as the metals of Group I and II and their oxides. Measurement of ionization energies of metal oxides is important as this allows accurate determination of exothermicities of charge exchange reactions involving metal oxides in the upper atmosphere.

A number of investigations have been undertaken as part of this report:-

1. The HeI photoelectron spectrum of scandium has been recorded in the gas-phase. Three bands associated with ionization from the outermost 3d and 4s orbitals have been observed and found to agree with ionization energies expected from optical data. The relative intensities of two of the bands, corresponding to 4s-ionization to the  $^3D$  and  $^1D$  states of  $Sc^+$ , have been investigated using an intermediate coupling model. Also, the  $\sigma_{3d}:\sigma_{4s}$  photoionization cross-section ratio has been measured at right angles to the photon beam giving a value of  $(57 \pm 12)$  at the HeI wavelength. A similar investigation has also been performed for titanium and vanadium. Again bands were observed

associated with  $(4s)^{-1}$  and  $(3d)^{-1}$  ionizations and a  $\sigma_{3d}:\sigma_{4s}$  photoionization cross-section ratio could be derived from the observed spectra. This investigation of titanium and vanadium in the gas-phase means that all the first row transition metals have now been investigated with HeI p.e.s. and as a result the variation of the  $\sigma_{3d}:\sigma_{4s}$  cross-section ratio along the transition series can now be presented (1).

2. Vacuum ultraviolet photoelectron spectra of vapor-phase SrO and BaO have been recorded and the spectra interpreted by ab initio molecular orbital calculations and Hartree-Fock-Slater calculations. The first band onsets of BaO and SrO have been measured as  $(6.46 \pm 0.07)$  and  $(6.60 \pm 0.05)$  eV respectively, and these lead to upper limits of the dissociation energies,  $D_0^0$ , in  $BaO^+(X^2\Sigma^+)$  and  $SrO^+(X^2\Sigma^+)$  of  $4.37 \pm 0.08$  and  $3.36 \pm 0.14$  eV (2).

In the initial stages of this work, some problems in recording photoelectron spectra were experienced because of chemi-ionization reactions of BaO and SrO with water. The chemi-electron spectra of these reactions have been investigated (2) and are important because reactions of this type represent ways of generating electrons in the upper atmosphere in the absence of ionizing radiation.

3. The photoelectron spectrum of  $Al_2O$ , obtained on evaporating mixtures of aluminium and aluminium oxide ( $Al_2O_3(s)$ ) has been obtained (3). Four bands were observed and this result, combined with the results of sophisticated molecular orbital calculations, indicate that this molecule is almost certainly linear in the vapour phase. As part of this study, the photoelectron spectrum of aluminium has also been recorded (3).
4. The He(I) photoelectron spectra of lithium, sodium and potassium hydroxide have been recorded and assigned using ab initio molecular orbital calculations (4). For all three hydroxides, bands associated with ionization of monomers and dimers were observed and these were identified by making use of superheating utilizing a double furnace assembly. For the monomers two bands were observed corresponding to



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the  $\text{MOH}^+(\text{X}^2\Pi) + \text{MOH}(\text{X}^1\Sigma^+)$  and  $\text{MOH}^+(\text{A}^2\Sigma^+) + \text{MOH}(\text{X}^1\Sigma^+)$  ionizations and from the observed band onsets, the heats of formation,  $\Delta H_f^\circ(298)$ , of the  $\text{MOH}^+(\text{X}^2\Pi)$  and  $\text{MOH}^+(\text{A}^2\Sigma^+)$  states were evaluated. These values were used to obtain the proton affinity of the alkali metal oxides, LiO, NaO and KO. The heats of formation of the cations,  $\text{MOH}^+$ , are important in determining exothermicities of possible reactions of these ions in the stratosphere.

5. The design and construction of a high temperature, high sensitivity photoelectron spectrometer has been achieved with partial AFOSR support (5, 6). This instrument uses an inductively heated furnace to produce atoms and molecules in the vapour phase at furnace temperatures in excess of 2000 K. Electrical interference is eliminated by using pulsed heating and gated electronics. A microchannel plate/phosphor screen/silicon-intensified-target camera detector is used for rapid data acquisition, to minimize problems caused by time dependent contamination in the ionization region. A dedicated, menu-driven, firmware-based data interface, with key-pad control, is utilized. TV monitoring of the photoelectron line images, and the use of a video window to select data, allow optimum spectral conditions to be preserved during an experiment. Results show reductions in data acquisition times of up to 90 compared to equivalent single channel detector experiments. Some results obtained with this spectrometer have been summarised in a recent publication (5).

6. In a study on NbO and TaO (7), in both cases four main bands were observed in the u.v. photoelectron spectrum which can be attributed to ionization of the isolated metal monoxide molecule. Bands associated with other oxides or the metal were not observed.

Assignment of the photoelectron spectra of NbO and TaO was made with the aid of Hartree-Fock-Slater (HFS) calculations and by comparison with the known photoelectron spectrum of VO. The first adiabatic ionization energies of NbO and TaO have been measured as  $(7.91 \pm 0.02)$  eV and  $(8.61 \pm 0.02)$  eV respectively. Suggestions were made to explain the poor agreement between previous mass-spectrometric values for the first ionization energy of each oxide and those measured in this p.e.s. study.

7. One of the main results of this project has been the demonstration that metal plus oxidant chemi-ionization reactions can be studied with electron spectroscopy. Some initial studies have been made, notably on the  $U + O_2$  and  $U + N_2O$ , and  $Ce + O_2$  reactions. For  $U + O_2$  and  $U + N_2O$  (8), both reactions exhibited one band in the electron spectrum. These bands have different band maxima and shapes which were rationalized using schematic potential energy surfaces and published mass spectrometric evidence. For the  $Ce + O_2$  reaction, again only one band has been observed which was again rationalised using schematic potential energy surfaces (9). Structure in the chemi-electron band was assigned to excitation of the  $\nu_1$  mode in  $CeO_2^+$ .
  
8. The isoelectronic molecules  $NCl$  and  $PF$ , both potential candidates for use in chemical laser systems, have been studied with u.v. photoelectron spectroscopy (10).  $NCl$  ( $a^1\Delta$ ) was prepared from the  $Cl + N_3$  reaction and  $PF$  ( $X^3\Sigma^-$ ) was prepared as a secondary product of the  $F + PH_3$  reaction. The adiabatic ionization energy for the process  $NCl^+(X^2\Pi) \leftarrow NCl(a^1\Delta)$  was measured as  $(9.69 \pm 0.02)$  eV and this has led to a determination of the first adiabatic ionization energy of  $NCl(X^3\Sigma^-)$  of  $(10.84 \pm 0.02)$  eV. The first adiabatic ionization energy of  $PF(X^3\Sigma^-)$  was measured as  $(9.60 \pm 0.01)$  eV. Spectroscopic constants,  $\bar{\omega}_e$  and  $r_e$ , in the ground  $^2\Pi$  states of the ions were determined as  $(1160 \pm 30) \text{ cm}^{-1}$  and  $(1.489 \pm 0.005) \text{ \AA}$  for  $NCl^+$  and  $(1030 \pm 30) \text{ cm}^{-1}$  and  $(1.498 \pm 0.005) \text{ \AA}$  for  $PF^+$  respectively. Assignments of the observed photoelectron bands have been supported by ab initio SCF-CI molecular orbital calculations.

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J.C.S. Faraday II 1987 (*in press*).



COMPLETED PROJECT SUMMARY

TITLE

Gas-Phase Photoelectron Spectroscopy  
of Metals and Metal Oxides of  
Importance in the Upper Atmosphere.

PRINCIPAL INVESTIGATOR

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INCLUSIVE DATES

1 September 1983 to 31 August 1987.

CONTRACT/GRANT NUMBER:

AFOSR-83-0283

COSTS AND FY SOURCE

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FY 86; \$19736 FY 87.

SENIOR RESEARCH PERSONNEL

Dr. A. Morris

JUNIOR RESEARCH PERSONNEL

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M.P. Hastings    V. Butcher  
G.D. Josland     A.E. Lewis  
M. Feher          M. Cockett  
A.J. Paul

## Publications

1. A Study of the Transition Metals; Scandium and Vanadium, with a new Multidetector Photoelectron Spectrometer.  
J.M. Dyke, M.P. Hastings, B. Gravenor, G.D. Josland and A. Morris  
J. Elec. Spec. Rel. Phen. 35, 1985, 65.
2. High Temperature Photoelectron Spectroscopy; A Study of SrO and BaO.  
J.M. Dyke, M. Feher, B. Gravenor and A. Morris  
J. Phys. Chem. 91, 1987, 4476.
3. High Temperature Photoelectron Spectroscopy; Al<sub>2</sub>O and Al.  
J.M. Dyke, M. Feher, M.P. Hastings, A. Morris and A.J. Paul  
Molecular Physics 58, 1986, 161.
4. High Temperature Photoelectron Spectroscopy;  
Study of LiOH, NaOH and KOH Monomers and Dimers.  
J.M. Dyke, M. Feher and A. Morris.  
J. Elect. Spec. Rel. Phen 41, 1986, 343.
5. A High Temperature Multidetector Photoelectron Spectrometer.  
J.M. Dyke, A. Morris, G. Josland, M.P. Hastings and P.D. Francis.  
High Temperature Science 22, 1986, 95.
6. High Temperature Photoelectron Spectroscopy;  
A Study of Niobium Monoxide and Tantalum Monoxide  
J.M. Dyke, A.M. Ellis, M. Feher, A. Morris, A.J. Paul and J.C.H. Stevens.  
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7. Properties of Gas-Phase Ions;  
Information to be obtained from Photoelectron Spectroscopy of Unstable Molecules.  
J.M. Dyke  
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V. Butcher, J.M. Dyke, A.E. Lewis, A. Morris and A. Ridha  
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9. Photoelectron Spectroscopy of Reactive Intermediates.

V. Butcher, M. Cockett, J.M. Dyke, A.M. Ellis, M. Feher, A. Morris and H. Zamanpour.

Phil. Trans. Roy. Soc. A 1987 (in press).

10. A Study of Chemi-ionization in the reactions  $U + N_2O$  and  $U + O_2$  with Electron Spectroscopy.

J.M. Dyke, A.M. Ellis, M. Feher and A. Morris.

Chemical Physics Letters 1987 (in press).

## Abstract of Objectives and Accomplishments

The objective of this research proposal was to use vacuum ultraviolet photoelectron spectroscopy to study in the gas-phase the electronic structure of a number of metals, metal oxides and metal hydroxides which are of importance in the upper atmosphere. High temperatures were required to produce the species of interest in the vapour phase and these were achieved with radiofrequency induction heating of a thin walled furnace containing a solid sample. The maximum temperature available was 3000 K. Experiments were performed both with a single detector high temperature photoelectron spectrometer and a multidetector high temperature instrument which was developed during the period of the grant.

Observation of the photoelectron spectra of a metal, metal oxide and metal hydroxide allows ionization energies to be determined accurately, relative photoionization cross-sections to be estimated and, for molecular species, if vibrational structure is observed, details of the ionic potential surface can be obtained. Of particular interest were the metals and oxides of the transition metals, lanthanides and actinides as well as the metals of Group I and II, their oxides and hydroxides.

Initially, attention was focussed on the first row transition metals. A study on scandium and vanadium completed a systematic investigation of the first row transition metals with ultraviolet photoelectron spectroscopy. Measurement of the relative band intensities observed in the photoelectron spectra of these metals allowed the  $\sigma_{3d}:\sigma_{4s}$  photoionization cross-section ratio to be measured at the photon energy used (21.22 eV). Once this study was completed a number of metal oxides were studied with photoelectron spectroscopy. They were:- BaO, SrO, TaO, NbO and Al<sub>2</sub>O. The information obtained from these studies can be illustrated by considering the SrO and BaO examples. In these cases, vacuum ultraviolet photoelectron spectra of vapour phase SrO and BaO have been recorded and the spectra interpreted using ab initio molecular orbital calculations and Hartree-Fock-Slater calculations. From the observed onsets of the first bands, values of the first adiabatic ionization energies have been derived as  $(6.62 \pm 0.10)$  eV for BaO and  $(6.76 \pm 0.05)$  eV for SrO. These values lead to dissociation energies,  $D_0^\circ$ , in  $BaO^+(X^2\Sigma^+)$  and  $SrO^+(X^2\Sigma^+)$  of  $(4.21 \pm 0.11)$  and  $(3.20 \pm 0.14)$  eV respectively.

Three hydroxides have also been studied as part of this work, LiOH, NaOH and KOH. For all three hydroxides, bands associated with ionization of monomers and dimers were observed and were identified by making use of superheating utilizing a double furnace assembly.

For the monomers, two bands were observed and from the observed band onsets, the heats of formation,  $\Delta H_{f(298)}$ , of the monomer ion  $X^2\Pi$  and  $A^2\Sigma^+$  states were evaluated. These values were used to obtain the proton affinity of the alkali metal oxides.

Some preliminary experiments have also been performed on the use of electron spectroscopy to study chemi-ionization reactions and a study has been completed on the  $U + O_2$  and  $U + N_2O$  reactions.

AFOSR Program Manager: Dr. Francis J. Wodarczyk.

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